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Peroxone mineralization of chemical oxygen demand for direct potable water reuse: Kinetics and process control

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ABSTRACT

Mineralization of organics in secondary effluent by the peroxone process was studied at a direct potable water reuse research treatment system serving an occupied four-bedroom, four bath university residence hall apartment. Organic concentrations were measured as chemical oxygen demand (COD) and kinetic runs were monitored at varying O_3/H_2O_2 dosages and ratios. COD degradation could be accurately described as the parallel pseudo-1st order decay of rapidly and slowly-oxidizable fractions, and effluent COD was reduced to below the detection limit (<0.7 mg/L). At dosages ≥4.6 mg L^{-1} h^{-1}, an O_3/H_2O_2 mass ratio of 3.4–3.8, and initial COD <20 mg/L, a simple first order decay was indicated for both single-passed treated wastewater and recycled mineral water, and a relationship is proposed and demonstrated to estimate the pseudo-first order rate constant for design purposes. At this O_3/H_2O_2 mass ratio, ORP and dissolved ozone were found to be useful process control indicators for monitoring COD mineralization in secondary effluent. Moreover, an average second order rate constant for $OH^{\bullet}$ oxidation of secondary effluent organics (measured as MCOD) was found to be $1.24 \times 10^7 \pm 0.64 \times 10^7$ M^{-1} S^{-1}. The electric energy demand of the peroxone process is estimated at 1.73–2.49 kW h electric energy for removal of one log COD in 1 m^3 secondary effluent, comparable to the energy required for desalination of medium strength seawater. Advantages/disadvantages of the two processes for municipal wastewater reuse are discussed.

1. Introduction

Water availability is becoming a challenging problem in many areas of the world due to shortage of freshwater sources, climate change, rapid population growth, increasing water demand and unsustainable consumption patterns. Therefore, new paradigms for water supply and management are needed. In particular, wastewater reuse has attracted increasing interest, because municipal wastewater is

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regarded as a stable and non-seasonal water source (Gong et al., 2008; Rivas et al., 2011; Englehardt et al., 2013). Reclaimed wastewater can be used in various applications, including for irrigation in urban and agricultural areas, as industrial process water, and for groundwater recharge. In fact, the United Nations Environment Programme classified wastewater reuse systems as "environmentally sound technologies when appropriately applied" (UNEP, 2006). Furthermore, the US National Research Council (2011) evaluated augmentation of national water supply through reuse of municipal wastewater, and reported that reclaimed water for potable water supply has significant potential to help meet future needs.

Generally, although conventional primary and secondary treatment can remove most contaminants in raw municipal wastewater, secondary effluent may contain a number of contaminants that are resistant to biological treatment. For example, when industrial wastewater constitutes a significant portion, advanced/tertiary treatment may be needed to meet the organic discharge limits (Ried et al., 2006). More commonly, many emerging organic compounds (EDCs), including pharmaceuticals and other endocrine disrupting compounds, are recalcitrant to biological degradation, and their occurrence in treated wastewater is often reported (Carballa et al., 2004; Lishman et al., 2006; Al-Rifai et al., 2007). Pharmaceuticals in particular cannot be easily regulated in terms of environmental half-life as pesticides and other hazardous organics are, and are being studied for potential ecological and human health impacts (Hernando et al., 2006; Bredhult et al., 2007). Therefore their removal prior to release may be desirable in water reuse applications such as irrigation, in which contaminants may accumulate in soils and in crops (Muñoz et al., 2009a; Snow et al., 2009). Removal is even more important for closed-loop water reuse systems. Here organics mineralization may be an attractive alternative to reverse osmosis (RO) treatment because it addresses the accumulation of pharmaceuticals and other persistent organic matter in the treated water and, in comparison with conventional treatment, the environment, and in any case represents an approach to direct potable water reuse when options for disposal of RO concentrate are not available locally. The highly oxidizing treatment regime is also expected to control the formation of disinfection byproducts. In fact, a Life Cycle Assessment study has indicated that such wastewater reuse employing advanced treatment appears as the best choice from both the ecotoxicity and global warming potential perspectives, when compared with reuse without tertiary treatment and with wastewater disposal/desalination supply (Muñoz et al., 2009b).

Among available advanced treatment technologies, advanced oxidation processes (AOPs), involving generation of hydroxyl radicals to achieve organics oxidation, are particularly attractive, as contaminants are permanently destroyed, not merely transferred to a brine or other phase for further treatment/disposal (Kusic et al., 2006). AOPs used for wastewater treatment include ozone-based processes, Fenton and photo-Fenton processes, photo-oxidation, photo-catalysis, electron beam irradiation and sonolysis (Vogelpohl and Kim, 2004). Among these, ozone-based treatment is one of the most practical because of its simplicity, strong oxidation potential, no toxic or hydrogen peroxide residual (with proper control of dosage) in the treated water, and relatively high energy efficiency compared with other technologies (Masten and Davies, 1994; Rosenfeldt et al., 2006). Ozone has been used in water and wastewater treatment for biological processes enhancement, metal removal, taste and odor removal and disinfection. Ozonation can also degrade pesticides and other micropollutants via direct or indirect pathways through the production of hydroxyl radical as a secondary oxidant. However, often ozonation alone is not enough, and the addition of H_2O_2 to accelerate generation of the more reactive hydroxyl radical via overall reaction

$$2O_3 + H_2O_2 \rightarrow 2OH^{\bullet} + 3O_2 \quad (1)$$

is necessary to achieve a high degree of mineralization (Kusic et al., 2006). In that case, the indirect reaction dominates in terms of organics mineralization.

Ozone/H_2O_2, often referred to as the peroxone process, has been used to treat ground water contaminated with TCE and PCE and remove atrazine and simazine from drinking water (Suty et al., 2004). Degradation of model hazardous pollutants such as phenol were reported (Esplugas et al., 2002) and several references report the application of peroxone treatment to secondary effluents (Rosal et al., 2008; Rivas et al., 2009). While peroxone represents a promising technology in terms of mineralizing organics for wastewater reuse, many questions remain as to process performance characteristics in real municipal wastewater matrices, given that water matrix is one of the most important factors in determining the kinetics and mechanisms of treatment (Tanaka et al., 2001; Domenjoud et al., 2011). For example, measured second order rate constants for hydroxyl radical oxidation of gross organics, e.g. as chemical oxygen demand or total organic carbon, in secondary effluent have not been available (as they are for natural organic matter). Further, in terms of water reuse, studies of the kinetics of peroxone oxidation in actual treated reuse water, which may not be reproducible in the laboratory, have not been available as a basis for design and economic analysis.

The present paper reports on the mineralization of contaminants by the peroxone process component of an urban net zero water treatment system operating at an occupied university residence hall apartment, to shed light on mechanisms in complex matrices and aid in process evaluation, system design and scale up, and cost estimation. COD was selected as the control parameter in this study because (a) the current urban net zero water treatment system was designed to produce high quality mineral water having a high concentration of total dissolved solids (TDS, >500 mg/L), several constitutes of which might interfere with TOC analysis; (b) COD measurement is less resource-intensive, allowing more frequent and complete monitoring; and (c) the stoichiometric COD/TOC ratio of a wastewater can approximate the molecular ratio of O_2 to C (2.66) although the actual correlation is determined by characteristics of the wastewater. Overall, COD is potentially a more "precautionary selection" as if the COD of treated water is below detection, one would expect a much lower TOC level. In addition, significant linear relationships between COD and TOC have been reported in municipal